Electronic and magnetic properties of some rare-earth dihydrides and dideuterides

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Résumé. — Les propriétés électroniques et magnétiques d'un certain nombre de dihydrures et dideutérures de terres rares ont été étudiées par spectroscopie Mössbauer. Dans les composés stœchiométriques ErH_2 et DyH_2 on a établi les détails de l'ordre magnétique et les niveaux fondamentaux de champ cristallin. Dans les composés non stœchiométriques DyH_{2+x} et (Er)HoH_{2+x} on observe les conséquences de l'abaissement de la symétrie ponctuelle au site des ions terre-rare induit par les distributions des sites d'hydrogène. Cet effet entraîne une augmentation des températures de transition magnétique et des distributions des moments magnétiques.

Abstract. — Mössbauer spectroscopy has been used to study the electronic and magnetic properties of a number of rare-earth dihydrides and dideuterides. In stoichiometric ErH_2 and DyH_2, magnetic transitions and crystal field ground states have been established. In non-stoichiometric compounds DyH_{2+x} and (Er)HoH_{2+x} changes of the rare-earth point symmetry due to distributions in hydrogen site occupations are seen. This results in increases in the magnetic transition temperatures and distributions in the magnetic moments.

The cubic rare-earth dihydrides (REH_2) have been studied by a variety of techniques for their interesting electronic and magnetic properties [1]. Susceptibility [2], inelastic neutron scattering [3, 4], specific heat [5] and Mössbauer experiments [6, 7] have been carried out to investigate the crystalline electric field (CEF) interactions. Knowledge of the CEF scheme allows a determination of the charge on the hydrogen atom since a reversal of the CEF level ordering will take place when the charge on the atoms surrounding the RE ion reverses sign. In addition, bulk magnetization and susceptibility [8] as well as Mössbauer effect studies [6] have explored the magnetic interactions and details of the magnetic ordering. The magnetic phenomena are of interest because these materials have large CEF interactions and weak magnetic coupling, even though they are good conductors. These tendencies are in contrast with those seen in rare-earth intermetallics.

In this paper we summarize results obtained from Mössbauer spectroscopy in a number of rare-earth dihydrides. The CEF and magnetic properties have been established for well defined stoichiometric compounds and compared to those inferred from other techniques. In addition, the striking consequences of hydrogen disorder arising from deviations in stoichiometry will be reported.

The rare-earth dihydrides crystallize in the fluorite structure over a relatively large composition range near REH_2 [1]. In this structure, the RE ions form a fcc lattice : there are both octahedral and tetrahedral sites available for the hydrogen ions. In stoichiometric compounds, one generally considers the tetrahedral sites to be fully occupied and the octahedral sites to be unoccupied. In such a situation, the rare-earth atom experiences a simple cubic CEF. Since there are only two CEF parameters involved, and the exchange field is weak, the electronic properties can be described with a limited number of parameters in terms of well known procedures [9]. We have performed Mössbauer effect measurements on stoichiometric ErH_2 using the 81 keV resonance in ^{166}Er, and on DyH_2 using the 26 keV resonance in ^{161}Dy.

In ErH_2 [6], the magnetic hyperfine field has been measured as a function of an external field in the paramagnetic region. Since the magnetic hyperfine field is strictly proportional to the electronic magnetic moment in rare-earth atoms, this provides a local magnetization measurement. The results are found to follow closely the calculated magnetization curve for a Γ_6 CEF ground state. When the temperature is lowered in zero field, a magnetic transition is observed at $T_N = 2.4 \pm 0.1$ K, and the saturation hyperfine field in the ordered state is again that expected for the Γ_6 state.

In stoichiometric DyH_2, Mössbauer and susceptibility measurements show the presence of a long-range antiferromagnetic ordering below $T_N = 3.3$ K [10]. The saturation hyperfine field unambiguously identifies a Γ_7 CEF ground state. A small electric quadrupole hyperfine interaction in the ordered state is accounted for by an admixture of excited CEF levels into the ground state through the exchange field. A combined crystal field and molecular field analysis was able to account for all

the hyperfine interactions with crystal field parameters (in the notation of ref. [9]) $W = 0.83 \pm 0.03$ K, $x = 0.24 \pm 0.02$ and an exchange field

$$H_{exc} = 26 \pm 5 \text{ kOe} .$$

The Schottky contribution to the specific heat calculated with these CEF parameters also gives excellent agreement with experiment [5]. For all the compounds discussed above, the CEF ground state is in agreement with there being negatively charged hydrogen atoms coordinated to the RE atoms.

The above discussion relies on the statement that the hydrogen atoms occupy fully and only the tetrahedral sites. However, if some of these sites are vacant and/or some of the octahedral sites are occupied, there may be profound effects on the magnetic properties. Consider DyH_2, where the cubic ground state has a magnetic moment of 3.78 μ_B. If a hydrogen vacancy appears in the near neighborhood of a Dy ion, the CEF symmetry will be lowered. This will necessarily have the effect of increasing the Dy magnetic moment. If a predominantly axial field develops, the moment will increase to a maximum value of 10 μ_B, with a resultant increase in the magnetic interactions. There is evidence that some disorder may exist between the octahedral and tetrahedral sites even in the stoichiometric compounds [11]. The Mössbauer spectra of DyH_2 [10] above the Néel temperature and the specific heat data [5] show a large amount of short-range magnetic order between 3.3 and 6 K. In the Mössbauer spectra this is revealed by a large distribution in hyperfine fields (and hence magnetic moments) with values always less than that corresponding to the Γ_7 ground state of Dy. The short-range order is attributed to some disorder in the hydrogen occupations which causes a larger moment on a small number of the Dy atoms ; these then serve as nucleation sites of the short-range order. As the temperature is lowered further, this situation is eventually overwhelmed by the long-range order that occurs between the majority (cubically coordinated) sites.

In non-stoichiometric compounds, the perturbation of the cubic CEF by the disorder in the hydrogen positions will be much more pronounced since one will necessarily have a significant proportion either of vacancies in the tetrahedral positions or of partial occupation in the octahedral sites. We have investigated non-stoichiometric compounds DyH_{2+x} having concentrations H/Dy = 1.94 and 2.14, and a deuterated compound with D/Dy = 1.96. In all cases, long-range order is seen with transition temperatures greater than that in the stoichiometric material. The largest transition temperature is observed for the greatest deviation from stoichiometry, i.e. for $DyH_{2.14}$, for which the transition temperature is about 20 K. In all cases, strong distributions of hyperfine fields are observed, reflecting the variation in CEF throughout the material due to the statistical nature of the hydrogen site occupations. Hyperfine fields as large as 5 MOe are seen in all three samples, thus directly showing the changes in the local symmetry and the resultant increase in the Dy magnetic moment. Similar phenomena have been observed by measurements on Er present as a dilute impurity in non-stoichiometric HoH_{2+x}. In view of the difficulty of controlling the stoichiometry of these materials, and the severe effects that can arise, it is important that great care be exercised in sample preparation for any studies.

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